



**PHYSICAL CHEMISTRY 2014**

12<sup>th</sup> International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry

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The Conference is dedicated to the  
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PHYSICAL CHEMISTRY 2014

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**PERRHENATE SORPTION BY AMINO-FUNCTIONALIZED GLYCIDYL METHACRYLATE COPOLYMER: INVESTIGATION OF RHENIUM AS AN ANALOGUE OF RADIOACTIVE TECHNETIUM**

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**ABSTRACT**

In order to define the favorable conditions for radioactive technetium (<sup>99</sup>Tc) uptake, the sorption behavior of its non-active chemical analogue rhenium (<sup>75</sup>Re) on amino-functionalized macroporous hydrophilic copolymer was studied. The pseudo-second-order (PSO) model provided the best fit for the kinetic data, while the intraparticle diffusion (IPD) model indicated a pronounced influence of the porous structure on the sorption rates. The maximum sorption capacity was found to be 84 mg g<sup>-1</sup> and 74 % removal efficiency was reached after 180 min in citrate buffer at pH 5.0.

**INTRODUCTION**

Tc-99 is a key constituent of nuclear waste produced in large quantities by nuclear fission of <sup>235</sup>U or <sup>239</sup>Pu in nuclear reactors. Its behavior can be predicted by investigating <sup>75</sup>Re, its excellent chemical analogue, owing to their similar electronic configuration, stereochemistry and thermodynamic properties, thus evading the use of a radioactive element at high concentrations i.e. doses [1]. Solvent extraction and ion exchange appear to be the most effective methods for the separation and removal of pertechnetate (<sup>99</sup>TcO<sub>4</sub><sup>-</sup>) and perrhenate (ReO<sub>4</sub><sup>-</sup>) from aqueous media [2]. Formerly successfully tested poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) grafted with diethylene triamine [PGME-deta] for <sup>99</sup>TcO<sub>4</sub><sup>-</sup> sorption at low concentrations [3], was the subject of this study as ReO<sub>4</sub><sup>-</sup> sorbent at high concentrations.

## EXPERIMENTAL

A macroporous PGME sample (with 40 mass% of crosslinker) was prepared by radical suspension copolymerization in the shape of spherical beads with the average particle diameter of 150-300  $\mu\text{m}$  and modified with diethylene triamine [PGME-deta] [3]. The copolymer sample was analyzed for its C, H, N content using the Vario EL III device (GmbH Hanau Instruments, Germany), and the amino group concentration was calculated (Table 1). The porosity parameters (for relevant abbreviations and definitions please consult Ref. [3,4]) were determined by high pressure mercury intrusion (Carlo Erba Porosimeter 2000, operating interval 0.1-200 MPa).  $\text{pH}_{\text{PZC}}$  was ascertained as published elsewhere [4].

Table 1. Relevant characteristics of PGME-deta [3,4].		pH dependence for $\text{ReO}_4^-$ sorption by PGME-deta was determined by monitoring Re(VII) uptake in the pH range of 1-13 in batch experiments, using appropriate buffer solutions [3]. The same mass of each sample (50 mg) was contacted with 1 $\text{cm}^3$ of $\text{NaReO}_4$ solution with the initial concentration of 5000 $\text{mg dm}^{-3}$ and 4 $\text{cm}^3$ of the buffer solution, at $T=298$ K. The sorption dynamics data was subsequently collected from deionized (DI) water adjusted to pH 5.0 with 0.1M HCl and from citrate buffer at pH 5.0. Re(VII) in supernatant was measured by ICP-OES Thermo Scientific CAP6000.
$S_{s,Hg}$ , $\text{m}^2 \text{g}^{-1}$	55	
$V_s$ , $\text{cm}^3 \text{g}^{-1}$	0.91	
$D_{V/2}$ , nm	107	
$D_{av}$ , nm	96	
Amino group concentration, $\text{mmol g}^{-1}$	5.01	
$\text{pH}_{\text{PZC}}$	7.8	

## RESULTS AND DISCUSSION

The  $\text{ReO}_4^-$  sorption dependence on pH (Figure 1a) was in concurrence with the previously established thesis that non-specific sorption of  $\text{ReO}_4^-$  happens via electrostatic interaction at the amine groups [1,3].

Table 2. Kinetic models.			Ref.	Determining the dynamics, specifically the rate of Re(VII) removal in the particular solid/solution system is one of the critical factors for the effective design of the sorption system [6]. With the aim to investigate the controlling mechanism of this sorption process, three kinetic models were applied to the experimental data, i.e. the
Kinetic model	Equation			
PFO	$\log(Q_e - Q_t) = \log Q_e - \frac{k_1 t}{\ln 10}$		[5]	
PSO	$\frac{t}{Q} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$	$h = k_2 Q_e^2$	[6]	
IPD	$Q_t = k_{id} t^{1/2} + C_{id}$		[7]	

pseudo-first (PFO), the pseudo-second order (PSO) and the intraparticle diffusion (IPD) model (Table 2) [5, 6, 7]. For relevant abbreviations and definitions in Table 2 please consult Ref. [5-7].

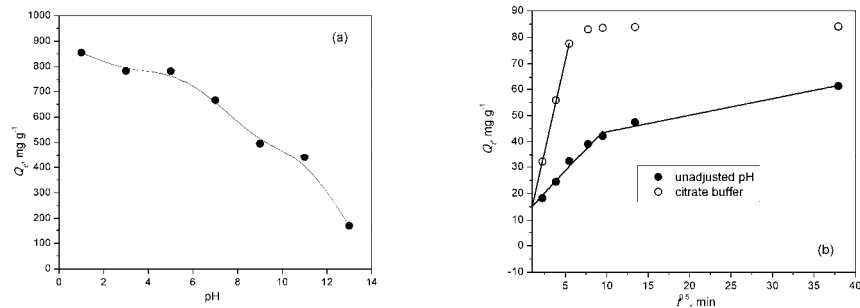
**Table 3.** Kinetic parameters for  $\text{ReO}_4^-$  sorption by PGME-deta ( $T=298\text{ K}$ ).

$C_i$ , $\text{mg L}^{-1}$	Unadjusted pH	Citrate buffer
$Q_e$ , $\text{mg g}^{-1}$	61	84
PFO		
$k_1$ , $\text{min}^{-1}$	0.00622	0.0355
$Q_e^{\text{calc}}$ , $\text{mg g}^{-1}$	38	33
$R^2$	0.901	0.845
PSO		
$k_2 \cdot 10^3$ , $\text{g mg}^{-1} \text{min}^{-1}$	0.488	3.349
$h$ , $\text{mg g}^{-1} \text{min}^{-1}$	1.91	23.3
$t_{1/2}$ , min	32.8	3.6
$Q_e^{\text{calc}}$ , $\text{mg g}^{-1}$	63	83
$R^2$	0.999	0.999
IPD		
$k_{1id}$ , $\text{mg g}^{-1} \text{min}^{-0.5}$	3.37	14.1
$C_{1id}$ , $\text{mg g}^{-1}$	11.8	0.886
$R^2$	0.976	0.999
$k_{2id}$ , $\text{mg g}^{-1} \text{min}^{-0.5}$	0.634	N/A
$C_{2id}$ , $\text{mg g}^{-1}$	37.4	N/A
$R^2$	0.980	N/A

PFO kinetic model was not appropriate for this system since  $R^2$  values were rather low. The theoretical  $Q_e^{\text{calc}}$  values calculated from PSO model are very close to the experimental  $Q_e$  values, with  $R^2=0.999$ . The best fit of PSO model implies that the sorption process is surface-reaction controlled, with chemisorption involving valence forces through sharing or exchange of electrons between PGME-deta and  $\text{ReO}_4^-$  [6].

To identify the influence of pore diffusion on sorption, the IPD equation was used (Figure 1b) [7]. The plots  $Q_t$  vs.  $t^{1/2}$  did not pass through the origin indicating that even though the sorption process

involved IPD, it was not the only rate-controlling step [7]. The positive value of  $C_{id}$  is indicative of some degree of boundary layer control [7].



**Figure 1.**  $\text{ReO}_4^-$  Sorption as function of pH (a) & intraparticle diffusion (b).

The removal efficiency in citrate buffer reached 74% in 180 min, while in DI water only 42% as the consequence of  $\text{pH}_{\text{PZC}}$  value shifting the pH of the

working solution towards neutral. Thus, in near neutral conditions, superb capacity can be achieved at high Re(VII) concentrations: 84 mg g<sup>-1</sup> in citrate buffer and 61 mg g<sup>-1</sup> in DI water adjusted to pH 5.0 after 24 h.

Very few papers deal with ReO<sub>4</sub><sup>-</sup> sorption and its kinetics. The maximum capacity of 60 mg g<sup>-1</sup> for quaternized 4-vinylpyridine and divinylbenzene resin [8], and 0.46 mmol g<sup>-1</sup> for chitosan modified carbon materials [9] were reported, which are comparable to the values presented in Table 3.

## CONCLUSION

The sorption behavior of one of the principal constituents of nuclear waste radioactive <sup>99</sup>Tc can be predicted by studying its non-active chemical analogue <sup>75</sup>Re. Thus, ReO<sub>4</sub><sup>-</sup> removal from aqueous solutions by amino-functionalized macroporous hydrophilic resin was studied in order to define the favorable conditions for <sup>99</sup>Tc uptake. Non-specific sorption of ReO<sub>4</sub><sup>-</sup> via electrostatic interaction at the protonated amine groups was demonstrated to occur most likely. PSO kinetic model fitted the kinetic data best, while IPD model revealed a pronounced influence of the porous sorbent structure on the sorption rates. Good removal efficiency of 74 % and maximum sorption capacity of 84 mg g<sup>-1</sup> were accomplished.

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